

DECOMPOSITION VOLTAGE

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Task 37

DECOMPOSITION VOLTAGE

I. Aim of the task

- examination of the impact of chemical changes taking place on the electrodes during electrolysis in the system: $\text{Pt} \mid \text{KBr} \mid \text{Pt}$ and the determination of the value of decomposition voltage,
- determination of the discharge potential of bromide ions on platinum covered with platinum black and testing the impact of bromide ions concentration in the solution for the potential value.

II. Introduction

1. Definitions: galvanic cells, electrolytic cells, half-cell, SEM cells, half-cell potential, standard half-cell potentials, EMF (electromotive force) cell.
2. Processes occurring at the electrodes under spontaneous conditions (working cell) and the forced (electrolyzer) flow of current; polarization of electrode; decomposition voltage; discharge potential; overpotential.
3. The process of electrolysis of the system $\text{Pt} \mid \text{KBr} \mid \text{Pt}$.

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III. Theory

III. 1. Definitions: galvanic cells, electrolytic cells, half-cell, SEM cells, half-cell potential, standard half-cell potentials, EMF cell

In electrochemical systems we are concerned with the processes and factors that affect transport of charges across the interface between chemical phases, for example, between an electronic conductor (a metal electrode) and an ionic conductor (an electrolyte). This is study of oxidation-reduction reactions involving the relationship between chemical energy and electrical energy. This process is carried out in an electrochemical cell consisting of electrodes dipped into an electrolyte.

Oxidation-reduction reactions or **redox** reactions are chemical reactions involving the transfer of electrons from one reactant to another. In such a reaction, two *half-reactions* occur; one reactant gives up electrons (undergoes oxidation) and the other reactant gains electrons (undergoes reduction). For example, a plate of zinc dissolves in a solution as zinc ions, with each Zn atom leaving 2 electrons, this is an example of an oxidation half-reaction.

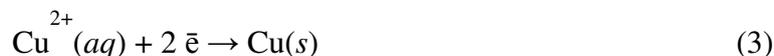


The oxidation number of Zn(s) is 0 and the oxidation number of Zn^{2+} is +2. Therefore, in this half-reaction, the oxidation number increases, this is another way of defining an oxidation. In contrast, the reverse reaction, in which Zn^{2+} ions gain 2 electrons to become Zn atoms, is an example of reduction.



In reduction there is a decrease in oxidation number. Chemical equations representing half-reactions have to be both mass and charge balanced. In the half-reactions above, there is one zinc on both sides of the equation. The charge is balanced because the 2+ charge on the zinc ion is balanced by two electrons, $2\bar{e}$, giving zero net charge on both sides.

Another example of reduction is the formation of solid copper from copper ions in solution.



In this half-reaction the oxidation number of ionic copper is +2, which decreases to 0 for the solid copper, and again charge and mass are balanced. However, no half-reaction can occur by itself. A redox reaction results when oxidation and reduction half-reaction are combined to complete transfer of electrons as in the following example:



The electrons are not shown because they are neither reactants nor products but have simply been transferred from one species to another (from Zn to Cu^{2+} in this case). In this redox reaction, Zn(s) is referred to as **the reducing agent** because it causes Cu^{2+} to be reduced to Cu. Cu^{2+} is called the **oxidizing agent** because it causes Zn(s) to be oxidized to Zn^{2+} .

III. 1.1. Electrochemical cells

Electrochemical cells consist of two electrodes: an anode (the electrode at which the oxidation reaction occurs) and a cathode (the electrode at which the reduction reaction occurs). There are two types of electrochemical cells: galvanic (spontaneously produces electrical energy) and electrolytic (consumes electrical energy).

III. 1.2. Galvanic cell or voltaic cell

A galvanic cell or voltaic cell are driven by a spontaneous chemical reaction that produces an electric current through an outside circuit. This cell is a device in which a redox reaction, such as the one in equation (4), spontaneously occurs and produces an electric current. For the transfer of electrons in a redox reaction, the electrons need to pass through an external electrically conducting wire instead of being directly transferred between the oxidizing and reducing agents. The design of a galvanic cell (shown in Figure 1 for equation (4) reaction) allows these phenomena to occur. In this cell, two solutions, one containing the ions of the oxidation half-reaction and the other containing the ions of the reduction half-reaction, are placed in separated compartments called *half-cells*. For each half-cell, the metal, which is called an *electrode*, is placed in the solution and connected to an external wire. The electrode at which oxidation occurs is called the *anode* [Zn in equation (4)] and the electrode at which reduction occurs is called the *cathode* [Cu in equation (4)]. The two half-cells are connected by a *salt-bridge* that allows a “current” of ions to pass from one half-cell to the other to complete the circuit of electron current in the external wires. When the two electrodes are connected to an electric load (such as a light bulb or voltmeter) the circuit is completed, the oxidation-reduction reaction occurs, and electrons move from the anode (–) to the cathode (+), producing an electric current. Figure 1. presents galvanic cell (or battery) based on the redox reaction in equation (4).

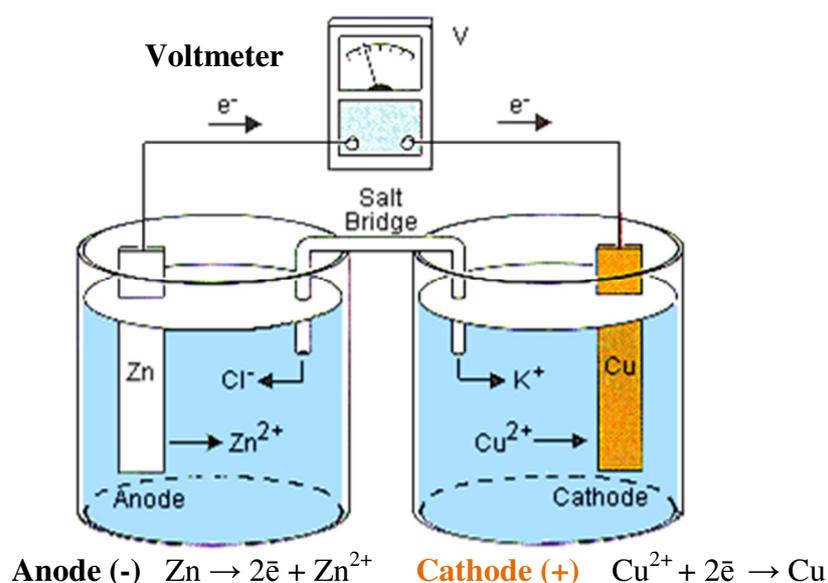


Fig. 1. Schematic diagram of a galvanic cell based on the redox reaction in equation [4].

The **cell potential**, E_{cell} , which is a measure of the voltage that the battery can provide, is calculated from the half-cell reduction potentials:

$$E_{cell} = E_{cathode} - E_{anode} \quad (5)$$

Under standard conditions, indicated by the superscript $^{\circ}$, the **standard cell potential**, E_{cell}° , is based upon the standard reduction potentials, as shown in equation (5).

$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} \quad (6)$$

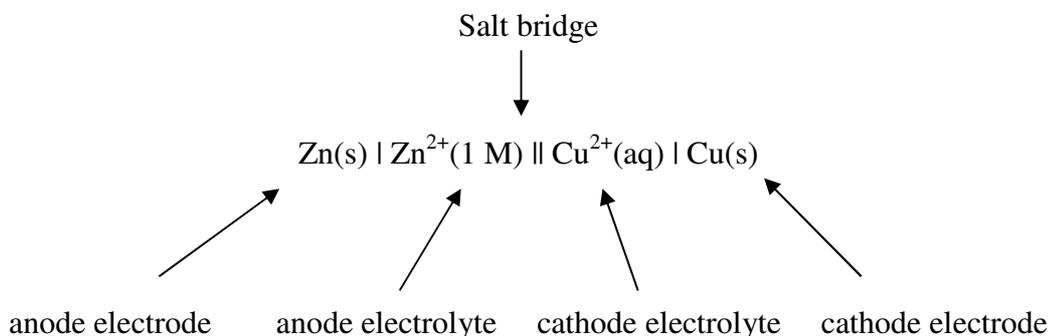
Electromotive force cell (efm), can be represented by the Nernst equation:

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} \ln(Q) \quad (7)$$

where: R - universal gas constant with a value of 8.314 [J/(K·mol)], T - temperature in [K], n - number of electrons in the overall reaction, F - Faraday constant with a known value of 96.500 [J/(V·mol)], Q - is the reaction quotient for the ion products/ion reactants of the cell.

Cell diagram

The cell diagram is the short-hand notation to represent the galvanic cell shown in Figure 1. If we assume the concentrations of both solutions are 1 M, then the cell diagram for the above galvanic cell is:



The single bar represents a phase boundary and the double bars the salt bridge. The anode compartment is followed by the cathode compartment, that are separated by salt bridge to indicate the direction of flow of electrons from anode to cathode.

III. 1.3. Electrolytic cells

Electrolytic cells, like galvanic cells, are composed of two half-cells, one is a reduction half-cell, the other is an oxidation half-cell. The direction of electron flow in electrolytic cells, however, can be reversed from the direction of spontaneous electron flow in galvanic cells, but the definition of both cathode and anode remains the same, where reduction takes place at the cathode and oxidation occurs at the anode. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed.

An idealized cell for the electrolysis of sodium chloride is shown in figure 2. A source of direct current is connected to a pair of inert electrodes immersed in molten sodium chloride. Because the salt has been heated until it melts, Na^+ ions flow toward the negative electrode and Cl^- ions flow toward the positive electrode.

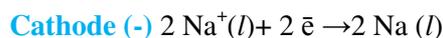
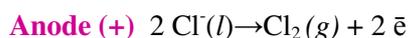
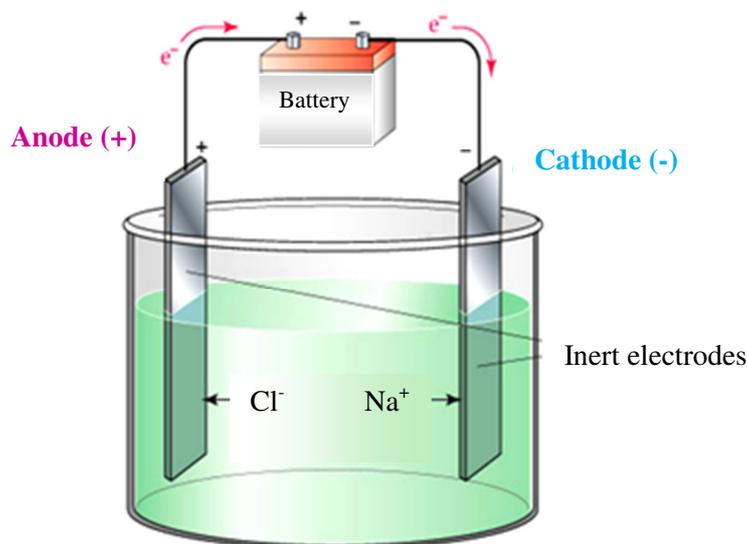


Fig. 2. Schematic representation of an electrolytic electrochemical cell.

When Na^+ ions collide with the negative electrode, the battery carries a potential large enough to force these ions to pick up electrons to form sodium metal.

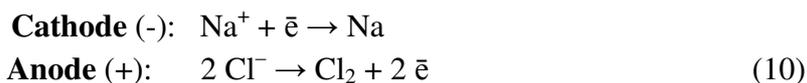


Cl^- ions that collide with the positive electrode are oxidized to Cl_2 gas, which bubbles off at this electrode.



The net effect of passing an electric current through the molten salt in this cell is to decompose sodium chloride into its elements, sodium metal and chlorine gas.

Electrolysis of NaCl:



III. 1.4. Differences between a Galvanic cell and an Electrolytic cell

Electrolytic cells are very similar to voltaic (galvanic) cells, both have a cathode and anode side, and both have consistent flow of electrons from the anode to the cathode. However, there are also striking differences between the two cells. The main differences are outlined in Table 1:

Table 1. Summary of differences between a galvanic cell and an electrolytic cell.

Electrochemical cell (Galvanic Cell)	Electrolytic cell
A galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
The redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The two half-cells are set up in different containers , being connected through the salt bridge or porous partition.	Both the electrodes are placed in a same container in the solution of electrolyte.
The anode is negative and the cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.	The anode is positive and the cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.	The external battery supplies the electrons. They enter through the cathode and come out through the anode.

III. 2. Overpotential

Let us analyze kinetic phenomena associated with the flow of current in a half-cell. If an electrode is in an equilibrium state than on the phase boundaries metal-solution, uniform current of exchange flows in both directions. By increasing the flow of current anode or cathode disturbing the equilibrium state, the process is irreversible. This phenomenon is called **electrolytic polarization**. Polarization of the electrodes can be the cause of both the flow of current from an external source, as well as its own cell current after closing the circuit. Electrodes, whose potential is a little changed under the influence of current flow, are called **non-polarizable electrodes**. This type of electrodes includes **calomel** and **hydrogen electrodes**, which are widely used in electrochemical studies. In contrast, the electrodes, whose potentials are subjected to a major change during the flow of current are called **polarized (e.g. noble metals like platinum Pt)**.

Consider the simple case of the half-cell of first (I) type with active electrode metal. Electrode processes running in the system can be divided into several stages:

- diffusion of ions from the bulk solution to the interface,
- desolvation of the solvate ions, to pass through the double layer,
- neutralization on the electrode surface,
- incorporation into the crystal network.

Each of these steps can inhibit the rate of the overall reaction of the electrode and change the electrode potential relative to its equilibrium potential E_{eq} [V]. This difference is called **the overpotential (overvoltage) η** [V]:

$$\eta = E - E_{eq} \quad (11)$$

where: E - electrode cell potential [V], E_{eq} - equilibrium potential [V].

If the diffusion is the slowest stage in the electrode process, we talk about the effect of concentration polarization and its contribution to the total overpotential is defined as the **concentration overpotential**. In contrast, the **activation overpotential** is connected with the charge exchange reaction.

To force the current flow through the electrolytic cell, applied voltage has to exceed the voltage at zero current at least by size of the cell overpotential. Overpotential of the cell is the sum of both half-cells overpotentials and ohmic voltage drop, resulting from the current flow through the electrolyte (resistance change in the diffusion layer of the electrolyte, the surface resistance protective layer on the electrode).

IV. Experimental

A. Devices and materials

1. Devices:

- electrolyzer EP-4,
- digital voltmeter,
- milliammeter,
- platinum electrodes coated with platinum black – 2 pcs.,
- saturated calomel electrode,
- measuring vessel,
- graduated pipette -10 and 25 cm³,
- measuring cylinder - 50 cm³.

2. Materials:

- 1 M KBr solution,
- 0.9 M KCl solution.

B. Determination of decomposition voltage

1. Installation of the measuring system

Reassemble the experimental set according to the scheme shown in Fig. 3. Before plugging into the electric network of the electrolyzer and the digital voltmeter **ask the demonstrator to check the measurement set**. Turn on the electrolyzer and the meter to the network for 15 minutes in order to warm up the device.

2. Performance electrolysis of the studied systems

Activate a magnetic stirrer turning the right knob "1". During the experiment the knob "2" should be twisted maximum to the right. Turning the knob clockwise leads the electrolyzer potentiometer "3" to gradually increase the voltage between the cathode and anode of a value **not greater than 0.1** (check on a digital voltmeter). After each change of voltage wait 0.5 min and after this time read the current intensity on the milliammeter.

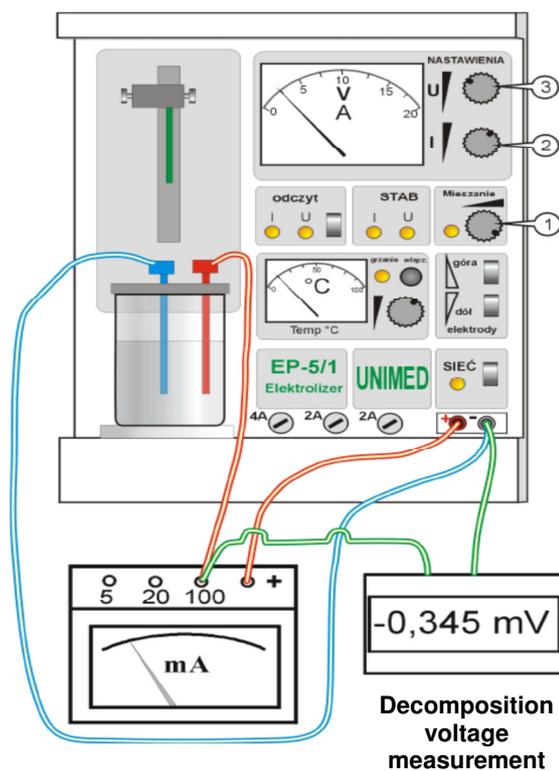


Fig. 3. Experimental setup [7].

3. Presentation of the measurement results

The measurement results should be presented in Table 2.

Table 2. Decomposition voltage measurement, T [K] =.....

No.	1M KBr	
	U [V]	I [mA]

C. Determination of discharge potential

1. Installation of the measuring system

Reassemble the experimental set according to the scheme shown in Fig. 4. Before plugging into the electric network of the electrolyzer and the digital voltmeter **ask the demonstrator to check the measurement set.**

2. Solutions

Electrolytic vessel should be filled successively with the studied solutions:

- 100 cm³ 1 M KBr,
- 10 cm³ 1 M KBr + 90 cm³ 0.9 M KCl

and the platinum electrodes as well as the saturated calomel electrode should be placed in it.

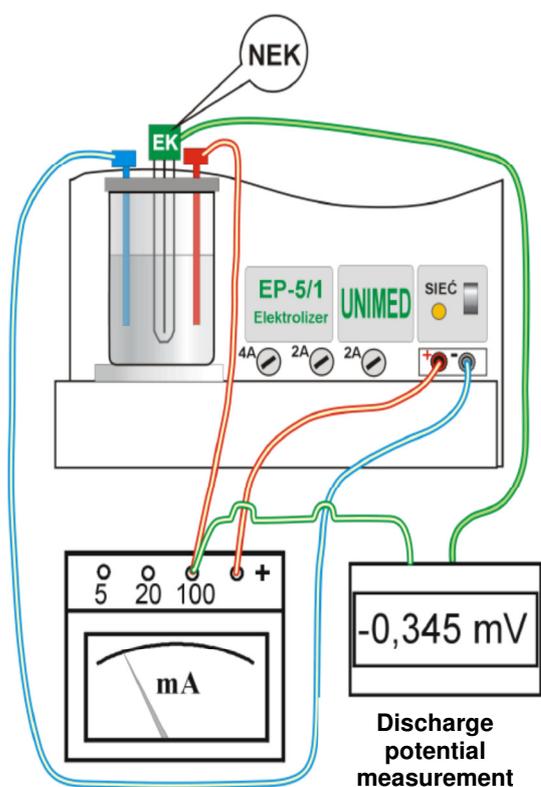


Fig. 4. Experimental setup [7].

3. Electrolysis

Make an electrolysis of the studied systems by measuring EMF cells $\text{Hg, Hg}_2\text{Cl}_2 \mid \text{KCl}_{(\text{SCE})} \mid \text{Br}^- \mid \text{Br}_2 \mid \text{Pt}$ and intensity of the current flowing in the circuit. Activate the magnetic stirrer turning the knob of the electrolyzer potentiometer "1" clockwise. By turning to the right the knob of potentiometer "3" gradually increase the voltage between the cathode and anode. After 0.5 minutes read the electromotive force (EMF) cell for $\text{Hg, Hg}_2\text{Cl}_2 \mid \text{KCl}_{(\text{SCE})} \mid \text{Br}^- \mid \text{Br}_2 \mid \text{Pt}$ on the digital voltmeter and current intensity on the

milliammeter. When the experiment is over, put the calomel electrode into the flask with a saturated solution of KCl.

4. Presentation of the results

The measurement results should be collected in Table 3.

Table 3. Measurement of discharge potential of bromide ions, T [K] =.....

No.	1M KBr		1M KBr + 0.9 M KCl	
	EMF [V]	I [mA]	I [mA]	EMF [V]

D. Calculations and Results

1. Determination of decomposition voltage

Voltage to be applied to the electrodes of the electrolyzer in order to force the flow of current intensity I is equal to:

$$U = U_o + IR + \eta \quad (12)$$

where: U_o - decomposition voltage, R - electrolyte resistance, η - sum of the anode and cathode overvoltage.

Because the discharge process of halogen ions is almost reversible on the glass electrodes, and hydrogen evolution overvoltage on the platinum electrode coated with platinum black is zero, we neglect the overvoltage term in eq. (12). Hence:

$$U = U_o + IR \quad (13)$$

The obtained measurement results should be present as a function $I = f(U)$. Then by extrapolation first calculate the decomposition voltage U_o .

2. Determination of discharge potential

a) Determination of the half-cell potential for $\text{Pt} | \text{Br}_2 | \text{Br}^-$.

EMF test cells can be present as potentials differences of $\text{Pt} | \text{Br}_2 | \text{Br}$ half-cell and calomel half-cell:

$$EMF = E = \Pi_{\text{Pt}/\text{Br}_2/\text{Br}^-} - \Pi_{\text{SCE}} \quad (14)$$

where: *SCE* - saturated calomel electrode

The potential of saturated calomel half-cell vs. the standard hydrogen half-cell is:

$$\Pi_{\text{SCE}} [\text{V}] = 0.2415 - 0.00076 (T - 298) \quad (15)$$

where: *T* - temperature [K].

From equation (14) and (15) calculate for a given temperature values of $\text{Pt} | \text{Br}_2 | \text{Br}^-$ half-cell potential.

b) Determination of bromide ions discharge potential.

Draw the curve of function $I = f(\Pi_{\text{Pt}/\text{Br}_2/\text{Br}^-})$ and define by extrapolation the value of discharge potential of bromide ions.

3. Conclusions

- describe the processes occurring during the electrolysis of the studied experimental systems.
- analyze the dependence of the potential discharge of bromide ions on their concentration in solution.